DEVELOPMENT OF MULTI-FUNCTIONAL AEROSPACE STRUCTURES USING CNT-MODIFIED COMPOSITE PRE-PREG MATERIALS

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Keywords: nanotubes, pre-preg, CFRP, multi-functionality

Abstract
In composites aerospace structures, there is a constant demand for multi-functional material solutions that provide enhanced electrical and thermal performance combined with increased mechanical performance, mainly concerning inter-laminar fracture characteristics. Such approaches are driven by the systemic design requirements of mass and cost reduction. The introduction on nanotechnology in the field of composites has opened new horizons towards this direction offering unique capabilities for the on demand tuning of the material properties. Nevertheless a key challenge yet exists to answer on the integration routes of nano-materials in already established and commonly used pre-impregnated fibrous reinforcements (pre-preg). This paper will review various technologies developed towards this direction under the framework of ELECTRICAL project.

1. Introduction
During the last decades, numerous research works reported that the incorporation of carbon nanotubes in carbon fiber reinforced composites –most commonly used in aerospace applications- influence positively and simultaneously various material properties (eg. mechanical, electrical, damping etc). In the R&D level, it is more that evident that the introduction on nanotechnology will lead the way towards the development of multi-functional aerospace composite structures. Moreover nanocomposites promise to offer unique capabilities for the on demand tuning of the material properties thus expanding even more the design flexibility using composites.

Almost 10 years later and numerous studies and promising scientific results that climaxed the expectations; it is evident to the engineering community that the technology of nanotubes modification to deliver multi-functional aerospace composite structures has reached a crucial milestone. This milestone is linked to the need to transform from lab scale -“preparation
environment”- to industrial scale -“production environment”. Only when this gap is bridged, solid benefits and practical applications of the technology are understood and accepted. Failing to do so may lead to a rejection of a technology by the industry. Concerning nano-modified FRP materials, a technology gap is identified between available nano-integration routes and already established FRP processing and manufacturing technologies to reach a seamless integration of nanotechnologies in production units.

Despite the increasing use of other composite manufacturing techniques (eg.RTM, infusion) in aerospace the pre-preg technologies consist yet the first choice of the majority of manufacturers. Pre-impregnated fibrous reinforcements (pre-preg) provide significant benefits over other solutions, such as the readiness to use with no further treatment, ease of handling, uniform fiber alignment, accurate control of the resin content, ability to conform to intricate shapes, optimum polymeric composites integration and very low void contents in the final products. Furthermore the recent advances in Out-of-Autoclave (OOA) pre-preg hold promise for fast and affordable aerospace composite manufacturing. Thus the integration of the nanotubes in commonly used pre-preg products is crucial especially when short term applications are considered. Aim of this work that was performed under the framework of FP7-ELECTRICAL project was to develop various nano-modification technologies for aerospace graded pre-preg systems.

1.1. Nano-modification Technologies

Under the framework of ELECTRICAL project, two (2) technologies were evaluated: Technology A refers to the direct CNT doping of the pre-preg resin system. The direct doping technology despite the fact that in the literature [1],[2] is mostly proposed and tested with some positive results, the parameters of the pre-preg processes are influencing the parameters of the nano-modification process (eg. CNT dispersion etc.). Furthermore from the perspective of the nano-modification for performance enhancement, the uniform distribution of the CNTs into the pre-preg resin matrix of the composite does not localize their beneficial effect in the areas that are mostly needed e.g. Inter-laminar regions. Technology B, comprise an effort to overcome aforementioned issue. Technology B refers to the treatment of conventional pre-preg materials by specific CNT deposition techniques using various CNT-carrier master-batches

1.2. Materials used and developed

The baseline pre-preg system selected for use in ELECTRICAL project was EF6809 and was provided by CYTEC, UK. In the case of Technology A, CYTEC shipped to AML-UoP a part A of EF6809 epoxy system. AML-UOP using high shear mixing techniques and an epoxy master-batch provided by ARKEMA, France produced a CNT doped part A of EF6809 to be returned back to CYTEC. The CNT-doped EF6809 full resin system created at CYTEC premises is used to produce CNT-DOPED EF6809 PRE-PREG that is delivered back to AML-UOP in resin film format. AML-UOP using suitable film lamination procedure produced CFRP composite laminates for testing. In the case of Technology B, CYTEC provided to AML-UOP an EF6809/IMS65 unidirectional carbon pre-preg of 600 mm width. AML-UOP using powder deposition techniques and epoxy master-batch of ARKEMA, France produced the CNT-TREATED EF6809 PRE-PREG. The new material was used within a classic pre-preg lamination procedure to produce CFRP composites laminates for testing.
The CFRP composites produced by both technologies were compared against reference materials produced using neat EF6809 resin film in the case of technology A and a conventional EF6809/IMS65 unidirectional carbon pre-preg for technology B. All materials produced were passed through production control that included volume fraction measurements and NDI via C-SCAN. The test matrix was developed in order to include mechanical, electrical and thermal performance characterization in order to investigate also the multifunctional aspect.

<table>
<thead>
<tr>
<th>Type</th>
<th>Material Property</th>
<th>Test Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>Mode 1 fracture toughness (G1c)</td>
<td>AITM-1-0005</td>
</tr>
<tr>
<td>Electrical</td>
<td>Through Thickness (Z) Electrical Conductivity</td>
<td>AITM-2-0065</td>
</tr>
<tr>
<td>Thermal</td>
<td>Through Thickness (Z) Thermal Conductivity</td>
<td>Mathis TCI</td>
</tr>
</tbody>
</table>

Table 2. Test Matrix followed.

2. Results and Analysis

In Table 3 the fiber volume fraction of the CFRP composites produced by both nano-modification technologies is summarized. The calculation was made using cured ply thickness (CPT) measurements from the plates produced. The CNT-DOPED EF6809 resin film (technology A) does not seem to affect the resulting fiber volume fraction. On the contrary the CNT-TREATED EF6809 prepreg (technology B) for the given curing procedure as in reference material results to composites with ~10% lower fiber volume fraction. The use of a carrier for the CNT to be deposited on the surface of the prepreg adds extra material that affects the volume fraction.

<table>
<thead>
<tr>
<th>Material:</th>
<th>TECHNOLOGY A</th>
<th>TECHNOLOGY B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>REFERENCE</td>
<td>NANO-DOPED</td>
</tr>
<tr>
<td>VOLUME FRACTION [%]</td>
<td>51±2</td>
<td>50±1</td>
</tr>
</tbody>
</table>

Table 3. Fiber volume fraction of the CFRP composites produced by both nano-modification technologies

In Table 4, the results from the characterization campaign are summarized for both technologies. It is evident that both nano-modification technologies provide an enhancement of the properties.

<table>
<thead>
<tr>
<th>Material:</th>
<th>TECHNOLOGY A</th>
<th>TECHNOLOGY B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>REFERENCE</td>
<td>NANO-DOPED</td>
</tr>
<tr>
<td>G1c (J/m2)</td>
<td>360±32</td>
<td>470±50</td>
</tr>
<tr>
<td>σz (S/m)</td>
<td>0,02±0,01</td>
<td>0,85±0,05</td>
</tr>
<tr>
<td>kz (W/mK)</td>
<td>0,53±0,01</td>
<td>0,60±0,05</td>
</tr>
</tbody>
</table>

Table 4. Summary of results from the characterization campaign for both technologies. [0]n type CFRP

As already identified by literature, direct CNT doping of the pre-preg resin system (technology A) provides notable (~30%) increase in the fracture toughness. Scanning electron
microscopy pictures from Mode I fractured specimens of the nano-doped material provide better insight for the mechanical bridging effect -in nano-scale- of carbon nanotubes.

![Microscopy pictures from Mode I fractured specimens of the nano-doped material](image)

**Figure 1.** SEM pictures from Mode I fractured specimens of the nano-doped material (technology A)

Furthermore thermal conductivity results verify that the presence of CNTs in the epoxy matrix does not contribute significantly to step change increase of the thermal performance linked mainly with filler content and epoxy-filler thermal resistance. Through thickness electrical conductivity is enhanced significantly verifying the suggestion that the CNTs most probably act as direct electrical bridges between neighboring carbon fibers when the fiber distance is stochastically at the same level with the effective length of the CNTs [3]. Nevertheless taking into account the low value recorded for the reference material and the fact that the performance is not exceeding 1 S/m - a common value in various applications - suggests that the potential for further enhancement of the electrical performance is probably limited. The
uniform distribution of the CNTs into the pre-preg resin thus matrix of the composite does not localize their beneficial effect in the areas that are mostly needed eg. inter-laminar regions.

The localized presence of the CNTs in the inter-laminar regions of the CFRP composites produced using the CNT-TREATED EF6809 pre-preg (technology B) seems to provide a beneficial impact to the out of plane electrical conductivity despite the lower volume fraction observed. Most possibly also the increase in the mode I fracture toughness recorded is linked the localized presence of CNTs that provide their mechanical bridging effect as observed in SEM analysis (Figure 2).

As in technology A, the thermal conductivity results verify that the presence of CNTs even localized does not contribute significantly to step change increase of the thermal performance. This observation once more confirms the assumption that thermal conductivity is linked mainly with filler content and epoxy-filler thermal resistance.
Figure 2. SEM observations on fractured specimens from composite plates produced using CNT-TREATED EF6809 pre-preg (technology B)

In order to further study the electric conduction mechanisms that are enabled in the unidirectional composites produced with CNT-TREATED EF6809 pre-preg (technology B), scanning electron microscopy analysis is performed on inter-laminar surfaces from specimens used for electrical conductivity were analyzed. In Figure 3 an instance of electrical bridging between fibers is shown.

Figure 3. SEM observations made on specimens used for electrical conductivity from composite plates produced using CNT-TREATED EF6809 pre-preg (technology B)
3. Conclusions

Two technologies for nano-modification of composite pre-preg processes were evaluated. From electrical performance point of view Technology B (CNT-TREATED EF6809 pre-preg) proved to provide high potential for enhancement of electrical performance most probably due to its localized deposition on the inter-laminar region. Moreover Mode I fracture toughness results indicate also beneficial effect also in terms of mechanical properties suggesting a multi-functional approach.

4. Acknowledgements

The research leading to these results has gratefully received funding from the European Union Seventh Framework Programme (FP7/2007- 2013) under Grant Agreement n° ACP0-GA-2010-265593 (ELECTRICAL). In addition, the authors acknowledge the work performed by all partners of the above mentioned project.

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